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PATENT SPECIFICATION

NO DRAWINGS

1,132,636

Date of Application and filing Complete Specification: 31 Aug., 1966.

No. 38754/66.

Application made in Italy (No. 21090) on 22 Sept., 1965.

Complete Specification Published: 6 Nov., 1968.

1,132,636

Index at acceptance:—A5 A1

Int. Cl.:—A 62 d 1/00

COMPLETE SPECIFICATION

Improvements in or relating to Flame-Extinguishing Compositions

We, MONTECATINI EDISON S.P.A., formerly Societa Edison, an Italian Company, of Foro Buonaparte 31, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to flame-extinguishing compositions and, more particularly, to those compositions based on completely halogenated fluorobromoalkanes and/or fluorobromochloroalkanes.

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PATENTS ACT, 1949

SPECIFICATION NO. 1,132,636

Reference has been directed, in pursuance of Section 9, subsection (1) of the Patents Act, 1949, to Patent No. 1,042,048.

THE PATENT OFFICE,
13th January, 1970

D 120743/2

not be utilized. The presence of the bromine atom in the molecule, with the easily broken bromine-carbon bond, causes these compounds to give rise to free radicals with extreme ease at relatively low temperatures; these free radicals interfering in the combustion process by stopping the chain-reactions deriving from the combustion itself. Moreover, the presence in these compounds of fluorine atoms, in place of the hydrogen and chlorine atoms present in more conventional extinguishing agents, increases their volatility, making them more efficacious, particularly at low temperatures; as well as stabilizing the radicals formed by scission of the bromine-carbon bond, so that these radicals cannot further decompose, thus

chlorofluorohydrocarbons and chlorofluorobromohydrocarbons, classified according to the system adopted by "Underwritters Laboratories".

[*Price 4s. 6d.*]

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This invention relates to flame-extinguishing compositions and, more particularly, to those compositions based on completely halogenated fluorobromoalkanes and/or fluorobromochloroalkanes.

The flame-extinguishing properties of the fluorobromoalkanes and fluorobromochloroalkanes are well known. Among all the known fluorobromoalkanes and fluorobromochloroalkanes, those which present the greatest interest from the industrial point of view are CF_2ClBr, CF_2Br_2, CF_3Br and $CF_2Br—CF_2Br$, as they have shown themselves to be the best among those till now tested. Such compounds are characterized by a high flame-extinguishing power. Furthermore, they are endowed with low toxicity and can therefore be used where other chemical extinguishing agents cannot be utilized. The presence of the bromine atom in the molecule, with the easily broken bromine-carbon bond, causes these compounds to give rise to free radicals with extreme ease at relatively low temperatures; these free radicals interfering in the combustion process by stopping the chain-reactions deriving from the combustion itself. Moreover, the presence in these compounds of fluorine atoms, in place of the hydrogen and chlorine atoms present in more conventional extinguishing agents, increases their volatility, making them more efficacious, particularly at low temperatures; as well as stabilizing the radicals formed by scission of the bromine-carbon bond, so that these radicals cannot further decompose, thus avoiding the formation of toxic reaction-products such as phosgene. Finally, their very high vapour density allows these fluorobromoalkanes and fluorobromochloroalkanes to be used even in the open air, as they remain over the combustion zone for a long time.

The fluorobromoalkanes and fluorobromochloroalkanes are also characterized by a relatively low toxicity, particularly in comparison with similar compounds also employed as flame-extinguishing agents, such as carbon tetrachloride, methylbromide and chlorobromomethane.

The table below lists toxicity data for chlorofluorohydrocarbons and chlorofluorobromohydrocarbons, classified according to the system adopted by "Underwritters Laboratories".

[Price 4s. 6d.]

Toxicity of some haloalkanes according to "Underwritters Laboratories" classification		Toxicity of some haloalkanes according to "Underwritters Laboratories" classification	
Compound	Class to which it belongs	Compound	Class to which it belongs
CCl_4	3	CBr_2F_2	4
CCl_3F	5a	$CBrF_3$	6
CCl_2F_2	6		
$CClF_3$	6	$CClBrF_2$	5a
CF_4	6	$CClF_3$	6
$CHCl_3$	3	$(CClBrF_2)$	5a
$CHCl_2F$	5	$(CBrF_3)$	6
$CHClF_2$	5a		
CHF_3	6	CH_3Br	2
		$(CBrF_3)$	6
$(CHCl_3)$	3	CH_2ClBr	3
(CCl_3F)	5a	$(CClBrF_2)$	5a
CH_2Cl_2	4—5		
$(CHCl_2F)$	5		
CCl_2F_2	6		

Since the toxicity of these products decreases in going from class 1 (to which sulphur dioxide belongs) to class 6 (to which $CBrF_3$ belongs), it may be seen that the fluorobromoalkanes and fluorobromochloroalkanes are characterized by a relatively low toxicity.

However, these fluorobromoalkanes and fluorobromochloroalkanes are not commercially available at a low price; and their use is seriously limited by their high manufacturing cost, even if their efficiency as flame-extinguishing agents is generally far higher than that of conventional extinguishing agents, such as carbon tetrachloride, methyl bromide and chlorobromomethane.

An object of the present invention is to provide extremely efficient flame-extinguishing compositions based on completely halogenated fluorobromoalkanes and/or fluorobromochloroalkanes.

The invention consists in a flame-extinguishing composition comprising at least one completely halogenated fluorobromoalkane and/or at least one completely halogenated fluorobromochloroalkane, together with one or more propelling and/or coadjuvant agents which are fluoroalkanes and/or fluorochloroalkanes and which each have at least one hydrogen atom in the molecule.

It has been found that the said fluorohydrocarbons or fluorochlorohydrocarbons when mixed with the completely halogenated fluorobromoalkanes or fluorobromochloroalkanes give compositions with a particularly high extinguishing power. More particularly, compositions according to the invention, wherein the propelling and/or coadjuvant agent comprises compounds having low toxicity, low boiling point, good solubility in the fluorobromoalkane or fluorobromochloroalkane and the capacity to give stable radicals by thermal decomposition, and whose molecules contain at least one hydrogen atom, are surprisingly endowed with a flame extinguishing power far higher than could be foreseen from the properties of their individual constituent components.

The compounds which, alone or in mutual combination, can be used in compositions according to the present invention as pro-

pelling and/or coadjuvant agents can be selected from a wide range of compounds whose molecules contain, besides carbon, fluorine and, where applicable, chlorine atoms, at least one atom of hydrogen (such as CF_2ClH; CF_3H, CF_2H_2, $CF_2H—CF_3H$).

The completely halogenated fluorobromoalkanes and fluorobromochloroalkanes which, alone or in mutual combination can be used as flame-extinguishing agents in the compositions according to the present invention can be selected from a wide range of compounds; and CF_2ClBr, $CF_2Br—CF_2Br$, CF_2Br_2 and CF_3Br are particularly suitable.

The proportion of propelling and/or coadjuvant agents to that of the actual extinguishing agents (completely halogenated fluorobromoalkanes and/or fluorobromochloroalkanes) in compositions according to the invention, depends on the nature of these compounds and can therefore vary within wide limits. Suitably, the molar ratio between the propelling and/or coadjuvant agent on the one hand, and the flame extinguishing agent on the other, may vary from 0.2 to 5.

The compositions according to the present invention can be used alone, or mixed with at least one substance having low toxicity and high stability, as an additional propelling agent. These additional substances can be selected from a wide range of compounds, particularly favourable results being obtained with compounds such as carbon dioxide and sulphur hexafluoride.

Further advantages and characteristics of the present invention will be apparent from the embodiments illustrated in the following Example.

EXAMPLE.

To determine the lowest concentration of the extinguishing composition in the air sufficient to prevent the spreading of the flames, an apparatus was used which is described in detail by E. C. Creiz in "Journal of research of the National Bureau of Standards" Volume 65 A No. 4 July—August 1961, page 389.

As fuel, propane was used, with a feed-rate between 150 and 250 cc/minute; and as supporter of combustion air was used with a feed-rate between 5 and 7 litres/minute.

In the following table data are listed showing the lowest concentration of the extinguishing agents in the air, at the moment of extinction of the flames.

For those compositions (numbered 7 to 9) which, according to the invention, comprise a mixture of a completely halogenated fluorobromoalkane and/or fluorobromochloroalkane with a propelling agent as hereinabove described, there is also shown the lowest effective concentration theoretically needed to extinguish the flames, calculated on the basis of the extinguishing properties of the constituents of the said mixture. The difference between the theoretical and actual lowest effective concentrations is also shown; as is the composition of these mixtures (in mol %). The compositions numbered 1 to 6 are shown for comparison purposes.

	Product	Composition in the liquid phase % (Mol)	Lowest concentr. in air at the moment of extinction % (mol)		Difference between the% theoretical and % actual
			Theoretical	Actual	
1	$CF_2Br\ CF_2Br$	99.7	—	0.8	—
2	CF_2Br_2	97	—	1.45	—
3	$CF_2Cl\ Br$	99.4	—	2.9	—
4	CF_2Cl_2	100	—	6.6	—
5	$CF_2Cl\ H$	99.6	—	11.9	—
6	$CF_2Cl\ Br$ CF_2Cl_2	54 46	4.6	4.6	0
7	$CF_2Cl\ Br$ $CF_2Cl\ H$	52 48	6.9	5	27.5
8	$CF_2\ Br—CF_2Br$ $CF_2\ Cl\ H$	50 50	6.1	1.75	71.5
9	CF_2Br_2 $CF_2Cl\ H$	47 53	6.5	1.45	78

From the data listed in the above table it can be seen how mixtures 7, 8 and 9, containing various fluorobromoalkanes or fluorobromochloroalkanes (as the actual extinguishing agents) and a fluorochlorohydrocarbon containing at least one hydrogen atom in the molecule, name (CF_2ClH), (as propelling and/or coadjuvant agent) show a flame extinguishing power far higher than that which could be expected from the properties of the constituent compounds. Conversely, for a given flame extinguishing power, the compositions according to the present invention entail a lower consumption of fluorobromoalkane or fluorobromochloroalkane than that indicated by theoretical consideration of the constituent compounds, this difference being as high as 78% in one case illustrated.

WHAT WE CLAIM IS:—

1. A flame-extinguishing composition comprising at least one completely halogenated fluorobromoalkane and/or at least one completely halogenated fluorobromochloroalkane, together with one or more propelling and/or coadjutant agents which are fluoroalkanes and/or fluorochloroalkanes and which each have at least one hydrogen atom in the molecule.

2. A composition as claimed in claim 1, in which the completely halogenated fluorobromoalkane component comprises one or more of the following compounds: $CF_2\ Br—CF_2\ Br$; CF_3Br; CF_2Br_2.

3. A composition as claimed in claim 1, in which the completely halogenated fluorobromochloroalkane is $CF_2\ Cl\ Br$.

4. A composition as claimed in any one preceding claim in which the propelling and/or coadjuvant agent comprises one or more of the following compounds: $CF_2\ Cl\ H$; CF_3H; $CF_2\ H—CF_2\ H$; $CF_2\ H_2$.

5. A composition as claimed in any one preceding claim, also comprising an additional propelling agent of low toxicity and high stability.

6. A composition as claimed in claim 5, in which the additional propelling agent is sulphur hexafluoride.

7. A composition as claimed in claim 5, in which the additional propelling agent is carbon dioxide.

8. A composition according to claim 1, as hereinabove described.

MARKS & CLERK,
Chartered Patent Agents,
Agents for the Applicants.

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Патент Великобритании № 1,132,636
31 авг. 1966 г.

Стр. 4, Формула изобретения

1. Пламягасящий состав, содержащий по меньшей мере один полностью галогенированный фторбромалкан и/или по меньшей мере один полностью галогенированный фторбромхлоралкан, вместе с одним, или более носителями и/или вспомогательными веществами, которыми являются фторалканы и/или фторхлоралканы и которые, каждый из них, имеют по меньшей мере один атом водорода в молекуле.

2. Состав по п. 1, отличающийся тем, что полностью галогенированный фторбромалкановый компонент содержит одно, или более веществ из числа следующих: CF_2Br $-CF_2Br$; CF_3Br; CF_2Br_2.

3. Состав по п. 1, отличающийся тем, что полностью галогенированным фторбромхлоралканом является CF_2ClBr.

4. Состав по любому одному из предыдущих п.п., отличающийся тем, что носитель и/или вспомогательное вещество содержит одно, или более веществ из числа следующих: CF_2ClH; CF_3H; CF_2H - CF_2H; CF_2H_2.